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Project Summary

EPA

Evaluation and Selection of Analytical Methods for Lawn-Applied Pesticides

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The work described in this report summarizes four different surveys that were conducted. The first two surveys were conducted to identify the lawn pesticides, including herbicides, insecticides, and fungicides, used in the Columbus, Ohio area by professional lawn care companies and home owners, respectively. The third survey was conducted to identify through literature publications available methods for analysis of 12 different lawn-applied pesticides that were identified in the first two surveys. The fourth survey, a literature search, was conducted to identify the major soil metabolites of four herbicide acids. Data from the two literature searches have been abstracted and compiled into separate databases using Borland's Paradox (DOS) software.

Methods reported in the literature may not be appropriate for anticipated EPA pesticide studies in track-in and intra-home redistribution. Published methods are not specific to the matrices of interest here (house dust, entryway soil, and polyurethane foam collected carpet and turf surface-dislodgeables). Potential interferences and co-extracted species such as humic acids, aliphatic fatty acids, lipids, phenols, PAH and other combustion source-derived species are not addressed.

This Project Summary was developed by EPA's National Exposure Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Various pesticides have been identified in house dust and indoor air. In at least one case, the presence in the home of several pesticides (e.g. chlorpyrifos, diazinon, o-phenylphenol) was clearly due to indoor use of whole room foggers and sprays. The presence of other pesticides appeared to be due to infiltration and migration into the home of pesticides that were originally applied to foundations, walkways, and gardens (e.g. permethrin, chlordane, heptachlor). Infiltration through foundation cracks probably explains the presence of chlordane indoors in many older homes and may be similar to radon infiltration. However, for pesticides such as permethrin, which are applied at sites distant from the foundation, track-in of contaminated soil on shoes may explain the presence of these outdoor-applied pesticides in the home.

House dust may be a more complex matrix than soil or plant material, as other human and combustion source-derived pollutants will be encountered (e.g. fatty acids, lipids, phenols, PAH, carpet additives). The ease in applying standard soil analysis methods to house dust samples for outdoor applied pesticides will be compromised further by pesticide levels that are expected to be significantly lower due to the dilution that occurs during any migration process. Therefore, methods suitable for outdoor levels are unlikely to be suitable for lower indoor levels in a specific matrix like house dust.

Conclusions

The primary lawn-care pesticides applied in the Columbus area are preemergence and post-emergence herbicides. The most frequently used preemergence herbicides are the dinitro-aniline derivatives pendimethalin, benfluralin, and trifluralin. The latter two are often combined in a mixture for application (trade name Team).

The most frequently used post-emergence herbicides are the acid herbicides, dicamba, 2,4-dichlorophenoxyacetic acid (2,4-D), mecoprop (or MCPP), and 2-methyl-4-chloro-phenoxyacetic acid (MCPA). Dicamba, 2,4-D, and mecoprop are frequently combined for application (trade name Trimec, among others). Recent concern over possible adverse health effects from 2,4-D exposure has prompted several of the larger lawn-care companies to replace the 2,4-D with MCPA in the Trimec or Trimec-equivalent formulations.

Applications of insecticides and fungicides vary widely in Columbus. These applications depend on the particular company and the general weather patterns. At least one company routinely applies an insecticide with herbicides. Mild winters and/or cool, wet weather increase the use of fungicides and insecticides. Other companies report that they have not applied fungicides in several years.

A previous study of pesticides in house dust stated that house dust extracts caused significant problems for "in control" GC quantification. Because problems of this nature were not identified in analyses of soil samples, we have to assume that soil and house dust are distinctly different in composition and that the complexity of house dust extracts requires more rigorous analytical methods, especially cleanup steps. Methods that have been reported in the literature cannot be recommended for anticipated pesticide studies in track-in and intra-home redistribution because they do not address the matrices of interest, do not provide sufficient cleanup steps, and, thus, do not have the requisite sensitivity. Published methods generally address the less complex matrices of soil and water.

From the standpoint of analysis methodology alone, the published methods 1) allude to difficulties in dealing with co-extracted humic acids without providing solutions, 2) provide little or no sample cleanup, 3) detail excessive artifact formation during derivatization steps, 4) obtain low recovery of analytes from clay-like soils, 5) provide insufficient detection limits, and/or 6) rely on relatively high-cost GC/MS analyses rather than lower-cost GC selective detector analyses.

Appropriate trace analysis methods need to be developed for the herbicide acids, the dinitro-aniline herbicides and moderately polar insecticides/fungicides, and glyphosate in house dust, entry-way soil, and dislodgeable residues. These methods need to address cleanup of co-extracted humic acids, fatty acids, lipids, and other neutral co-extracted organics. Target detection limits of 10-100 ppb in dust and soil are anticipated for studies of the migration of lawn-applied pesticides. Extraction methods developed for dust and soil need to be compatible with the PUF polymeric structure, so that only a simple scaling factor is needed to adapt dust methods to PUF-collected surface-dislodgeables. Proposed analysis methods for dust and soil are detailed in this report.

The literature survey of herbicide acid soil metabolites indicated that major metabolites are either acidic or phenolic species. For the chlorophenoxy herbicide acids (2,4-D, mecoprop, and MCPA) the dominant metabolite is the phenol that results after cleavage of the alkanoic side chain (e.g. 2,4-dichlorophenol from 2,4-D). Because of the similarity in polarity between herbicide and metabolite, both species may be analyzed using a single method. This approach is routinely used in studies of glyphosate, where both parent and its metabolite, aminomethylphosphonic acid, are monitored.

Recommendations

We recommend that the analysis methods proposed in this report be evaluated for application to the respective pesticide classes with regard to recovery, precision, and accuracy in the three matrices of interest. The analysis methods should be evaluated for detection and quantification at trace (10-100 ppb) levels in house dust, high clay content entry-way soil, and PUF-collected surface dislodgeables.

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The complete report, entitled "Evaluation and Selection of Analytical Methods for Lawn-Applied Pesticides," (Order No. PB96-199559; Cost: $25.00, subject to change) will be available only from:
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